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VIBRATIONAL SPECTROSCOPY WITH ANGLE-DEPENDENT EELS: ACETYLENE C-ETC(U)

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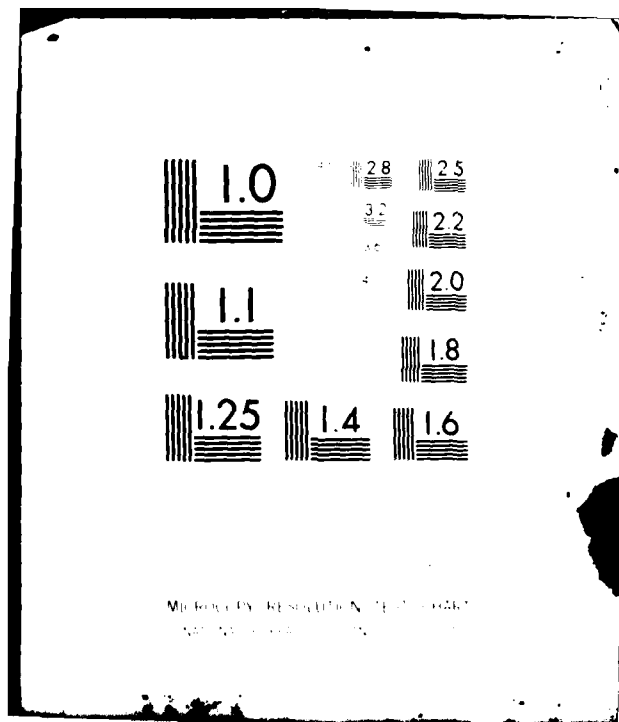
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VIBRATIONAL SPECTROSCOPY WITH ANGLE-DEPENDENT EELS:

ACETYLENE CHEMISORPTION ON Pd(111)

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SURFACE VIBRATIONAL SPECTROSCOPY WITH ANGLE-DEPENDENT EELS:

ACETYLENE CHEMISORPTION ON Pd(111)

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Abstract

High resolution electron energy loss measurements and LEED observations for normal and deuterated acetylene chemisorbed on Pd(111) are reported. Analysis of specular and off-specular energy loss data permits classification of the vibrational modes in terms of long-range dipole and short-range impact scattering mechanisms. Impact scattering intensities are found to be relatively strong for some modes and comparable in strength to intensities of dipole-excited modes. The vibrational data indicates that chemisorbed acetylene is strongly rehybridized ( $\sim sp^{2.5}$ ), in approximate agreement with earlier photoemission work. Comparison is made to vibrational assignments for  $C_2H_2$  chemisorbed on Ni(111) and Pt(111) as well as relevant model compounds. A surface bonding geometry is proposed which involves acetylene coordination at threefold sites on the Pd surface in the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure.

## I. Introduction

A popular theme in modern surface science investigations has been the study of atomic and molecular adsorption on single crystal surfaces under well-defined experimental conditions. Such systems may provide important insight and information on various aspects of catalyzed surface reactions<sup>1</sup>. A major area of investigation has been hydrocarbon adsorption and reactivity on transition metal surfaces, and a wide variety of surface sensitive techniques have been applied to these studies including ultraviolet photoemission spectroscopy (UPS), low-energy electron diffraction (LEED), thermal desorption spectroscopy (TDS) and high-resolution electron energy loss spectroscopy (EELS)<sup>2</sup>. In this paper we present and interpret angle-dependent EELS results for the vibrational spectra of acetylene ( $C_2H_2$ ) chemisorbed on Pd(111) at low temperature ( $\sim 150K$ ). We find that the chemisorbed acetylene molecule is strongly rehybridized, and we postulate a model surface bonding geometry. Relevant to our work here we cite recent photoemission<sup>3</sup> and EELS<sup>4-7</sup> work for  $C_2H_2$  chemisorption on (111) surfaces of Ni, Pd, Pt and Rh.

A critical aspect of EELS vibrational analysis has involved the electron energy loss mechanism. It is now recognized that in addition to a long-range dipole scattering mechanism the short-range "impact" scattering mechanism is important as well. Dipole scattering theory showed that the scattering is strongly peaked in the direction of specular reflection and that only modes which have a dynamic dipole moment perpendicular to the surface may be observed on specular (surface dipole selection rule)<sup>8</sup>. However, with the initial observation of off-specular impact scattering for H on W(100)<sup>9</sup> and more recent studies on hydrocarbons<sup>5,10</sup>, the importance of impact scattering has become increasingly apparent. Impact scattering is dominant in the gas phase<sup>11</sup> due to various resonance processes. Such resonances have been reported very recently

for several physisorbed molecules<sup>12</sup>. A theoretical framework to treat several important aspects of surface impact scattering has been developed by Tong, Li, and Mills<sup>13</sup>. In the present work we present a rather detailed angular analysis of the energy loss spectra for chemisorbed  $C_2H_2$  and  $C_2D_2$ , allowing an approximate classification of modes excited by dipole and impact mechanisms. Only by such analysis can symmetry arguments based on the surface dipole selection rule be applied with confidence.

## II. Experimental

The experimental apparatus consisted of an ion-pumped stainless-steel vacuum system (base pressure  $\sim 1 \times 10^{-10}$  Torr) equipped for EELS, LEED, Auger spectroscopy, ion-sputtering and quadrupole mass spectrometry. Liquid nitrogen cooling was used to obtain a nominal sample temperature of 150K in these experiments. The preparation and cleaning of the Pd(111) sample and sample dosing have been previously described<sup>10</sup>. Purified  $C_2H_2$  (99.6%) from Matheson and  $C_2D_2$  (99%) from Merck and Co. were used in these measurements and were examined mass spectroscopically. Precautions were taken against acetone impurity in the  $C_2H_2$  by passing the gas through a dry-ice cooled molecular sieve trap. Sample exposures cited here have been corrected for ion-gauge sensitivity.

The high-resolution electron spectrometer has been described earlier<sup>14</sup>. In these experiments the resolution (FWHM) of the elastic beam varied between 10 and 12 meV ( $\sim 80$ – $100$   $cm^{-1}$ ) at count rates of  $\sim 10^5$  Hz. Care was taken that this resolution and analyzer transmission was essentially maintained over the entire spectral range ( $0$ – $3200$   $cm^{-1}$ ). Spectra were obtained by digital scanning and data acquisition with an LSI-11 microcomputer, except for initial spectrometer tuneup which employed X-Y recorder display of the ratemeter output versus analyzer slit voltage.

Off-specular measurements were performed by rotation of the sample about an axis perpendicular to the plane of electron beam incidence, while holding the angle between the monochromator and analyzer fixed. The angular FWHM of the elastic beam was found to be approximately  $4^\circ$  by this procedure. For the condition of specular beam analysis the incident beam angle was  $65^\circ$  from the surface normal.

### III. Results

EELS spectra and LEED patterns have been examined as a function of  $C_2H_2$  exposure over a range of 0.5-2.0 L ( $1L=10^{-6}$  Torr-sec) at  $T=150K$ . In Figure 1 we show the EELS vibrational spectra as a function of exposure for  $C_2H_2$  in the specular direction. Features attributed to the  $C_2H_2$  adsorbate occur at 500, 673, 872, 1034, 1402, and  $2992\text{ cm}^{-1}$  as well as a small, broad peak due to CO impurity near  $1800\text{ cm}^{-1}$ . As shown in Figure 1 we find that the spectral intensities saturate near 1.5 L exposure, and we find no evidence for a significant change in the adsorbate over the exposure range examined. One notes, however, some changes in relative intensities of the loss peaks as a function of coverage.

LEED observations parallel the EELS data in the sense that a weak  $(\sqrt{3} \times \sqrt{3})R\ 30^\circ$  diffraction pattern is seen at 0.5 L exposure which grows in intensity up to 1.5-2.0 L exposure. This pattern was readily visible but the fractional-order spots were diffuse, indicative of relatively small domains of ordered  $C_2H_2$ . We also note, but do not discuss in detail here, that warming of the adsorbate to  $\sim 200K$  results in irreversible changes in the EELS spectra and is accompanied by disordering of the  $(\sqrt{3} \times \sqrt{3})R\ 30^\circ$  LEED pattern. Warming the  $C_2H_2$  adsorbate to 300K leads to at least partial conversion of  $C_2H_2$  to the ethynylidyne ( $\text{C}\equiv\text{C}-\text{CH}_3$ ) molecule<sup>10</sup>. Details of the thermal evolution of  $C_2H_2$  and  $C_2H_4$  on Pd(111) will be discussed elsewhere<sup>15</sup>.

The results illustrated in Figure 1 and our LEED observations indicate that the  $C_2H_2$  overlayer is fully developed at approximately 1.5 L exposure. Most

spectra were taken at this exposure because of the relatively intense loss features. We present here spectra taken at an electron beam impact energy of  $E_0 = 3.8$  eV, which was found to give relatively high elastic and inelastic count rates. We have also examined the impact energy dependence of the energy loss features<sup>16</sup>, but we do not discuss this aspect in detail here. We note, however, that marked changes in relative intensities of certain loss features occur as a function of electron beam energy, consistent with the differing excitation mechanisms of dipole and impact scattering discussed below.

We now turn to discussion of specular and off-specular EELS data. The off-specular data is important for two reasons: (i) it may provide symmetry information on the adsorbate by identifying those loss features which are dipole-enhanced and those which are predominantly impact excited; (ii) weaker loss features, not readily apparent on specular, may often be resolved off-specular. In the present study over 30 complete spectra were obtained for each of the adsorbates  $C_2H_2$  and  $C_2D_2$  in an angular range of  $-15^\circ$  to  $+15^\circ$  from the specular beam direction. In Figures 2-3 we illustrate representative specular and off-specular data for  $C_2H_2$  and  $C_2D_2$ . In Figure 2 for  $C_2H_2$  we note the relative intensity change between the peaks at  $673\text{ cm}^{-1}$  and  $872\text{ cm}^{-1}$  and the relative change in strength of the  $2992\text{ cm}^{-1}$  loss. These relative intensity changes are mimicked in the  $C_2D_2$  spectra (Figure 3) for the corresponding loss features at  $511\text{ cm}^{-1}$ ,  $621\text{ cm}^{-1}$ , and  $2249\text{ cm}^{-1}$ . We note that the  $C_2D_2$  spectra are somewhat complicated by the presence of a small amount of  $C_2H_2$  as confirmed by a weak loss peak near  $3000\text{ cm}^{-1}$  (CH stretch). Although such  $C_2H_2$  may possibly be formed by HD exchange from residual surface hydrogen we believe it more likely to arise from  $C_2H_2$  background impurity during sample exposure to  $C_2D_2$ . In Figure 3 we identify only those spectral features which we were able to clearly attribute to  $C_2D_2$  by analysis of a large number of spectra.

The results of the off-specular analysis are summarized in Figure 4. Here we show absolute intensities measured for the principal  $C_2H_2$  and  $C_2D_2$  loss features as a function of angle from specular. The interpretation of these angular profiles is based on the result that vibrational modes which are dipole-enhanced should exhibit a strongly pronounced specular lobe of narrow angular width<sup>8</sup>. The actual angular width in our experiments is approximately governed by the (instrumental) width of the elastic beam, shown in the top panel of Figure 4. Vibrational modes which exhibit broad angular behavior are attributed to a short range impact scattering mechanism. We emphasize that these arguments do not imply that modes which are allowed by the surface dipole selection rule will always exhibit strong dipole enhancements. In some cases the dynamic dipole moment may be sufficiently small that impact scattering contributions dominate<sup>17</sup>.

Based on the above arguments we determine from Figure 4 that for  $C_2H_2$  the modes at  $673\text{ cm}^{-1}$  (CH bend) and  $1402\text{ cm}^{-1}$  (CC stretch) are dipole enhanced. We also note that the modes of the deuterated species closely resemble the corresponding  $C_2H_2$  modes both in angular behavior and in absolute intensity. Such a correspondence was also used to advantage by Ibach and Lehwald for  $C_2H_2$  on Ni(111).<sup>5</sup> We further identify the modes at  $872\text{ cm}^{-1}$  ( $621\text{ cm}^{-1}$ ) and  $2992\text{ cm}^{-1}$  ( $2249\text{ cm}^{-1}$ ) as being impact excited. These modes exhibit a much broader angular behavior than the dipole-enhanced modes, the mode at  $2992\text{ cm}^{-1}$  (CH stretch) being essentially flat<sup>18</sup>. Because of a slight peaking on specular one may argue for some dipole enhancement of the  $872\text{ cm}^{-1}$  ( $621\text{ cm}^{-1}$ ) mode but such behavior is permissible for impact scattering as well. Finally, we mention that additional weaker loss peaks were found at  $500\text{ cm}^{-1}$  and  $1034\text{ cm}^{-1}$  for  $C_2H_2$  and tentatively identified ca.  $850\text{ cm}^{-1}$  for  $C_2D_2$ , but reliable angular data for these low intensity modes was not obtainable. In Table 1 we summarize the observed

frequencies for  $C_2H_2$  and  $C_2D_2$ , the dominant excitation mechanisms, and the probable mode assignments discussed in Section IV.

In closing this section we emphasize two aspects of the angular-dependent EELS data not discussed above. First, although we have identified certain modes as being "dipole enhanced" we note that these modes also have significant contributions from non-dipole (impact) mechanisms. For example, if we make the rough approximation that the intensities from two mechanisms are simply additive and, furthermore, that the impact scattering is independent of angle we may estimate the relative strength of the two mechanisms. We find by this very rough calculation that each of the modes at  $1402\text{ cm}^{-1}$  ( $\nu_{CC}$ ) and  $673\text{ cm}^{-1}$  ( $\rho_{CH}$ ) derive ~85% of their intensity on specular from dipole scattering. Secondly, we point out the considerable relative strength of the impact excited modes, even on specular. The modes at  $872\text{ cm}^{-1}$  and  $2992\text{ cm}^{-1}$  for  $C_2H_2$  are perhaps the strongest impact excited modes (in a relative sense) yet observed for a chemisorbed molecule. Other examples have been reported for hydrocarbons, especially for  $\nu_{CH}$  modes<sup>5,10</sup>.

#### IV. Discussion

In this section we discuss the vibrational mode assignments for  $C_2H_2$  chemisorbed on Pd(111) and compare to other spectroscopic information on this system, relevant molecular analogues and corresponding data for Ni(111) and Pt(111). We note that a rather extensive ultraviolet photoemission study of  $C_2H_2$  and  $C_2H_4$  was carried out by Demuth<sup>3</sup> on (111) surfaces of Ni, Pd, and Pt whereas EELS vibrational data was reported for Ni and Pt by Demuth, Ibach, and Lehwald<sup>4-6</sup>. Felter and Weinberg<sup>19</sup> have recently summarized various aspects of the photoemission and EELS work on Ni and Pt and have discussed appropriate chemisorption models.

The vibrational mode assignments given in Table 1 for  $C_2H_2$  on Pd(111) are based on deuteration shifts, angular variation of the loss intensities and comparison to relevant molecular analogues. The presence of the  $\nu_{CH}$  mode at  $2992\text{ cm}^{-1}$  and the  $\nu_{CC}$  mode at  $1402\text{ cm}^{-1}$  confirms that the molecular geometry is strongly distorted from the free ( $sp$  hybridized)  $C_2H_2$  ground state. By comparison with gas phase hybridization data<sup>20</sup> on the  $\nu_{C-H}$  and  $\nu_{C-C}$  frequencies we conclude that the  $C_2H_2$  molecule is approximately  $sp^{2.5}$  hybridized with a C-C bond length of  $1.42 \pm 0.03\text{\AA}$ . This geometry is in reasonable agreement with the estimated C-C bond length of  $1.34\text{--}1.39\text{\AA}$  given by Demuth<sup>3</sup> on the basis of an approximate photoemission analysis. However, the photoemission analysis was unable by itself to rule out a class of weakly distorted acetylene structures<sup>3</sup>.

Although we may safely conclude that the molecular geometry for  $C_2H_2$  on Pd(111) is strongly distorted, further conclusions on surface geometry are speculative and rely heavily on comparison to model compounds, such as organometallic complexes. However, these compounds rarely serve as ideal models and vibrational data is frequently sparse. To our knowledge, the most relevant compound for  $C_2H_2$  for which vibrational analysis is available is  $C_2H_2(Co)_2(CO)_6$ .<sup>21</sup> In this compound the C-C bond length is estimated as  $1.37\text{--}1.39\text{\AA}$ , the acetylene probably adopting a  $\mu$ -bridging geometry<sup>21</sup>. It is also of interest to compare to vibrational frequencies of electronically excited states of  $C_2H_2$ <sup>22</sup>, as emphasized recently by Felter and Weinberg<sup>19</sup>. In Table 2 we summarize relevant vibrational data on these systems as well as EELS chemisorption work. Since the most complete (angular-dependent) EELS analyses are available for Ni<sup>5</sup> and Pd we rely most heavily on these comparisons. The  $\nu_{CC}$  and  $\nu_{CH}$  frequencies clearly indicate a stronger molecular distortion for the case of Ni( $-sp^{2.7}$ ). However, we find a remarkable similarity between the reported frequencies and isotopic shifts for the  $\delta_{CH}$  and  $\rho_{CH}$ <sup>23</sup> bending modes for  $C_2H_2$  on Pd(111) and Ni(111). This may suggest a similar surface bonding

geometry for  $C_2H_2$  on the two surfaces. We also note favorable correspondence between certain vibrations for  $C_2H_2$  on Pd(111) and the excited ( $^1A_u$ ) state of acetylene. (The trans-bent  $^1A_u$  state is probably not favored for chemisorption but the cis-bent excited state is expected to have similar frequencies<sup>19</sup>.) Excellent correspondence in the  $\nu_{CC}$  frequencies for  $C_2H_2$ /Pd(111) and the di-cobalt complex is evident but the  $\nu_{CH}$  modes are  $\sim 100\text{ cm}^{-1}$  higher in the complex. We take this as some evidence that the chemisorbed acetylene is somewhat more distorted on the Pd(111) surface than in the di-cobalt complex and is coordinated to more metal atoms.

We conclude this discussion with speculation on the possible surface geometry for  $C_2H_2$  on Pd(111). By utilizing the vibrational assignments and assigned scattering mechanisms (Table 1) one may place some restrictions on the point group symmetry of the chemisorbed acetylene. If one considers the first layer of palladium atoms only then one may have acetylene surface geometries of  $C_{2v}$  and  $C_2$  symmetry, but the highest symmetry is  $C_s$  if second layer interactions are significant. However, in the case of  $C_{2v}$  symmetry, neither of the  $\rho_{CH}$  modes would be dipole enhanced, contrary to our EELS observations. Furthermore, the fact that one of the  $\rho_{CH}$  modes ( $872\text{ cm}^{-1}$ ) is apparently not dipole enhanced, argues in favor of a geometry with  $C_s$  or  $C_2$  symmetry. We cannot, however, rigorously rule out lower symmetry ( $C_1$ ) structures since the dynamic dipole moment of the  $872\text{ cm}^{-1}$  mode may simply be relatively small.

To summarize, we favor a structure with  $C_s$  or  $C_2$  symmetry, and the former seems most likely if second layer interactions are significant. The strong distortion ( $\sim sp^{2.5}$ ) and our estimated C-C bond length of  $1.42\text{\AA}$  is suggestive of the bonding of acetylenic ligands in trinuclear transition-metal complexes. We cite, for example, the  $Os_3(CO)_{10}(C_2Ph_2)$  compound where the C-C bond length is  $1.44\text{\AA}$  and the molecule is symmetrically coordinated near the center of the metal

triangle<sup>24</sup>. Figure 5 illustrates this suggested surface geometry for  $C_2H_2$  in the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure. In this model the C-C axis lies parallel to the surface and the molecular plane of the cis-bent  $C_2H_2$  (CCH angle  $\sim 122^\circ$ ) is slightly tilted relative to the surface normal as indicated. This model has  $C_s$  symmetry and is consistent with the fact that the  $\rho_{CH}$  (asym.) mode does not show dipole enhancement. We also note that the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure exhibits rather close-packing of the acetylene molecules as shown by the approximate Van der Waals radii<sup>25</sup>. Certainly, many other models are possible including various tilted C-C axis and trans-bent configurations. More definitive analysis will require detailed normal coordinate calculations for model surface geometries.

#### Acknowledgements

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Table 1. Assignment of the vibrational modes, frequencies ( $\text{cm}^{-1}$ ) and excitation mechanisms for  $\text{C}_2\text{H}_2$  on Pd(111) at  $T=150\text{K}$ . Standard deviations of measured frequencies are generally less than  $10 \text{ cm}^{-1}$ .

<u><math>\text{C}_2\text{H}_2</math></u>	<u><math>\text{C}_2\text{D}_2</math></u>	<u><math>\nu_{\text{H}}/\nu_{\text{D}}</math></u>	<u>Dominant Mechanism</u>	<u>Mode Assignment</u>
2992	2249	1.33	impact	$\nu_{\text{CH}}^{\text{d}}$
1402	1359	1.03	dipole	$\nu_{\text{CC}}$
1034	850 <sup>a</sup>	1.22	(c)	$\delta_{\text{CH}}$
872	621	1.40	impact	$\rho_{\text{CH}}$ (asym.)
673	511	1.32	dipole	$\rho_{\text{CH}}$ (sym.)
500	(b)	--	(c)	$\nu_{\text{Pd-C}}$

<sup>a</sup>Weak loss peak assigned to the region  $840\text{--}860 \text{ cm}^{-1}$ .

<sup>b</sup>Not resolved.

<sup>c</sup>Not determined.

<sup>d</sup>Symmetric and asymmetric modes too close to resolve.

Table 2. Comparison of vibrational mode assignments and frequencies ( $\text{cm}^{-1}$ ) for free (ground and first excited state), complexed, and chemisorbed acetylene on (111) surfaces of Ni, Pd, and Pt. Frequencies given in parentheses for deuterated molecules.

Vibrational Mode	$\text{C}_2\text{H}_2^a$ ( $1\Sigma_g^+$ )	Excited $\text{C}_2\text{H}_2^b$ ( $1A_u$ )	Complexed <sup>c</sup> $\text{C}_2\text{H}_2\text{Co}_2(\text{CO})_6$	Chemisorbed		
				$\text{C}_2\text{H}_2/\text{Pd}(111)$	$\text{C}_2\text{H}_2/\text{Ni}(111)^d$	$\text{C}_2\text{H}_2/\text{Pt}(111)^e$
$\nu_{\text{CH}}$ (sym.)	3374 (2701)	--	3116 (2359)	2992 (2249)	2920 (2190)	3010 (2245)
$\nu_{\text{CH}}$ (asym.)	3287 (2427)	3020 (2215)	3086 (2297)			--
$\nu_{\text{CC}}$	1974 (1762)	1380 (1310)	1403 (1347)	1402 (1359)	1220 (1190)	1310 (1260)
$\delta_{\text{CH}}$ (sym.)	612 (505)	--	768 (602)	1034 (850)	1080 (890)	985 (730)
$\delta_{\text{CH}}$ (asym.)	729 (539)	1049 (844)	894 (751)	--	1370 (1090)	--
$\rho_{\text{CH}}$ (sym.)	--	--	--	673 (511)	690 (540)	770 (570)
$\rho_{\text{CH}}$ (asym.)	--	--	--	872 (621)	860 (640)	--
$\nu_{\text{M-C}}$	--	--	605 (561) 551 (520)	500 (--)	560 (--) 480 (460)	570 (--) 340 (310)

<sup>a</sup>Herzberg, Ref. 20, ground state.

<sup>b</sup>Ingold et al., Ref. 22, first electronically excited singlet state (trans-bent).

<sup>c</sup>Iwashita et al., Ref. 21.

<sup>d</sup>Ibach and Lehwald, Ref. 5.

<sup>e</sup>Ibach and Lehwald, Ref. 6.

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16. L.L. Kesmodel and J.A. Gates, to be published.
17. This is seen to be the case here for the  $\nu_{CH}$  modes of  $C_2H_2$  and was observed for the  $\nu_{CH_3}$  modes of  $(\geq C-CH_3)$  on Pd(111)<sup>10</sup>.
18. This peak is believed to consist of both symmetric and asymmetric  $\nu_{CH}$  modes which lie too close to be resolved. These modes are separated by only 30  $cm^{-1}$  in the dicobalt acetylene complex.
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Figure Captions

- Fig. 1. Electron energy loss spectra for  $C_2H_2$  on Pd(111) as a function of  $C_2H_2$  exposure.
- Fig. 2. Electron energy loss spectra for  $C_2H_2$  on Pd(111) for specular and off-specular scattering.
- Fig. 3. Electron energy loss spectra for  $C_2D_2$  on Pd(111) for specular and off-specular scattering.
- Fig. 4. Absolute intensities of energy losses as a function of the angle  $\Delta\theta$  from specular for primary beam energy of 3.8 eV. Note the close similarity in angular behavior and absolute intensity for the corresponding modes of  $C_2H_2$  and  $C_2D_2$ .
- Fig. 5. Proposed bonding geometry for  $C_2H_2$  on the Pd(111) surface in the  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure. In this model the carbon atoms are located near threefold surface sites with the C-C axis parallel to the surface and the H atoms in a cis-bent configuration ( $C_s$  symmetry). Oval shaped areas are approximate regions of Van der Waals repulsion.

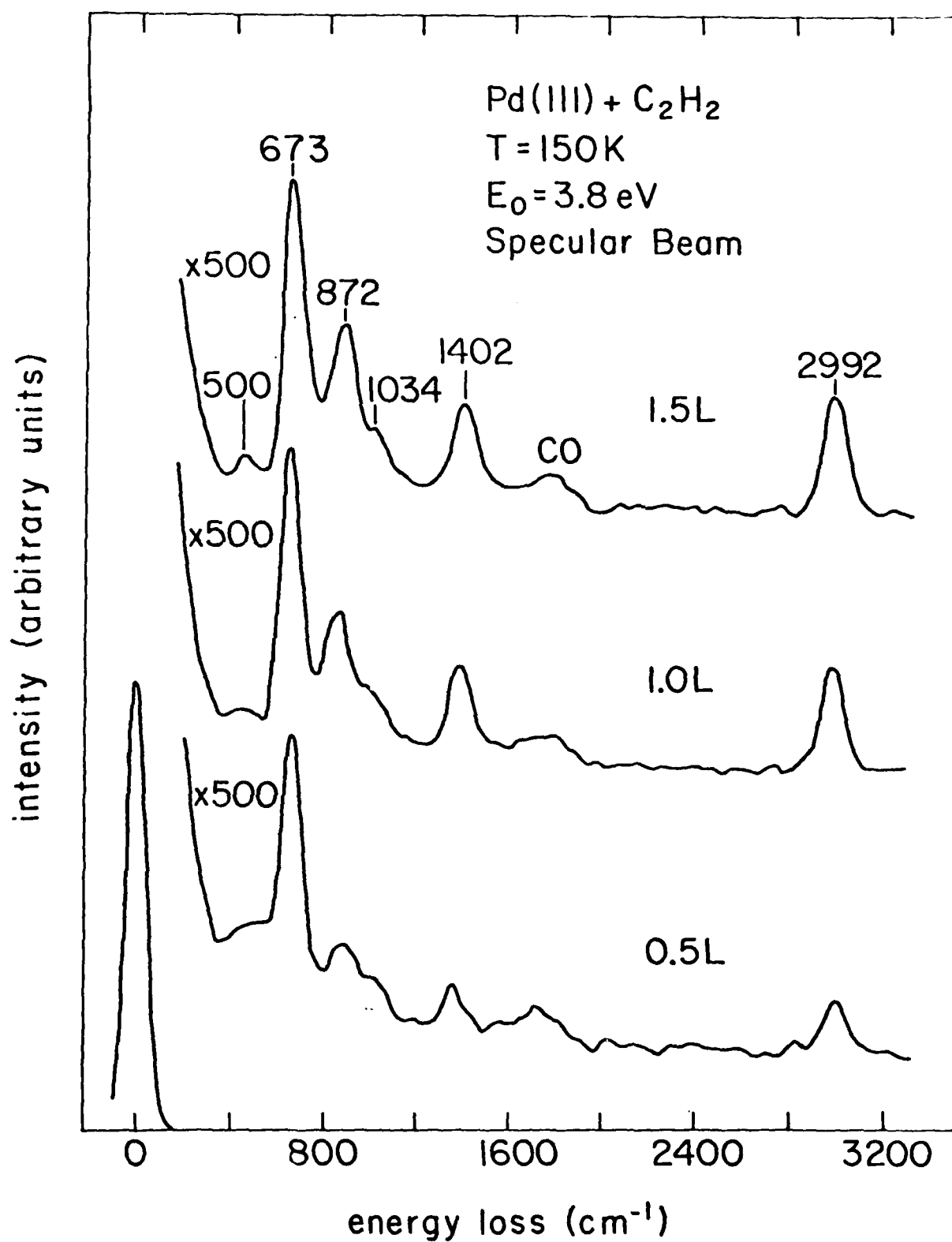


FIGURE 1

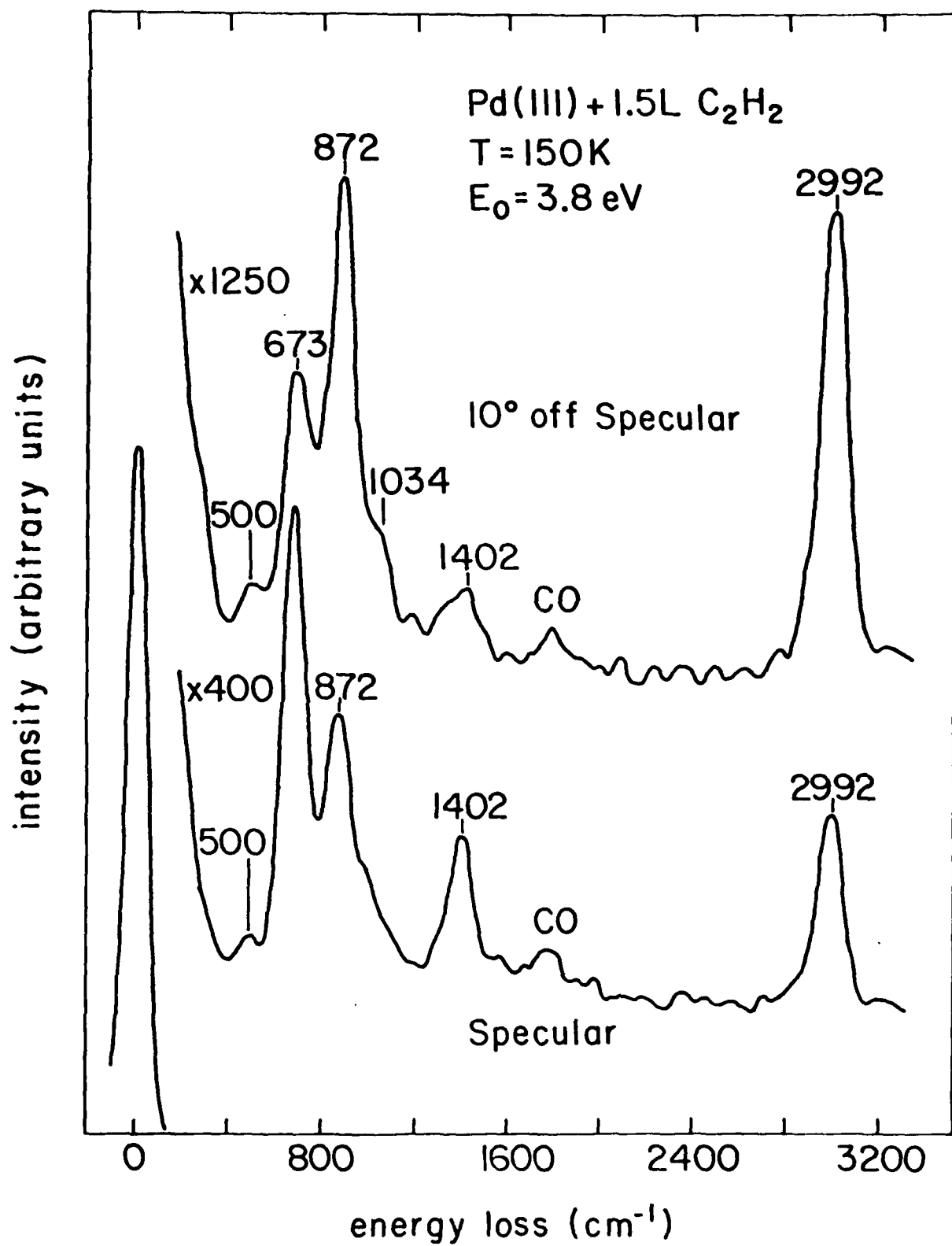


FIGURE 2

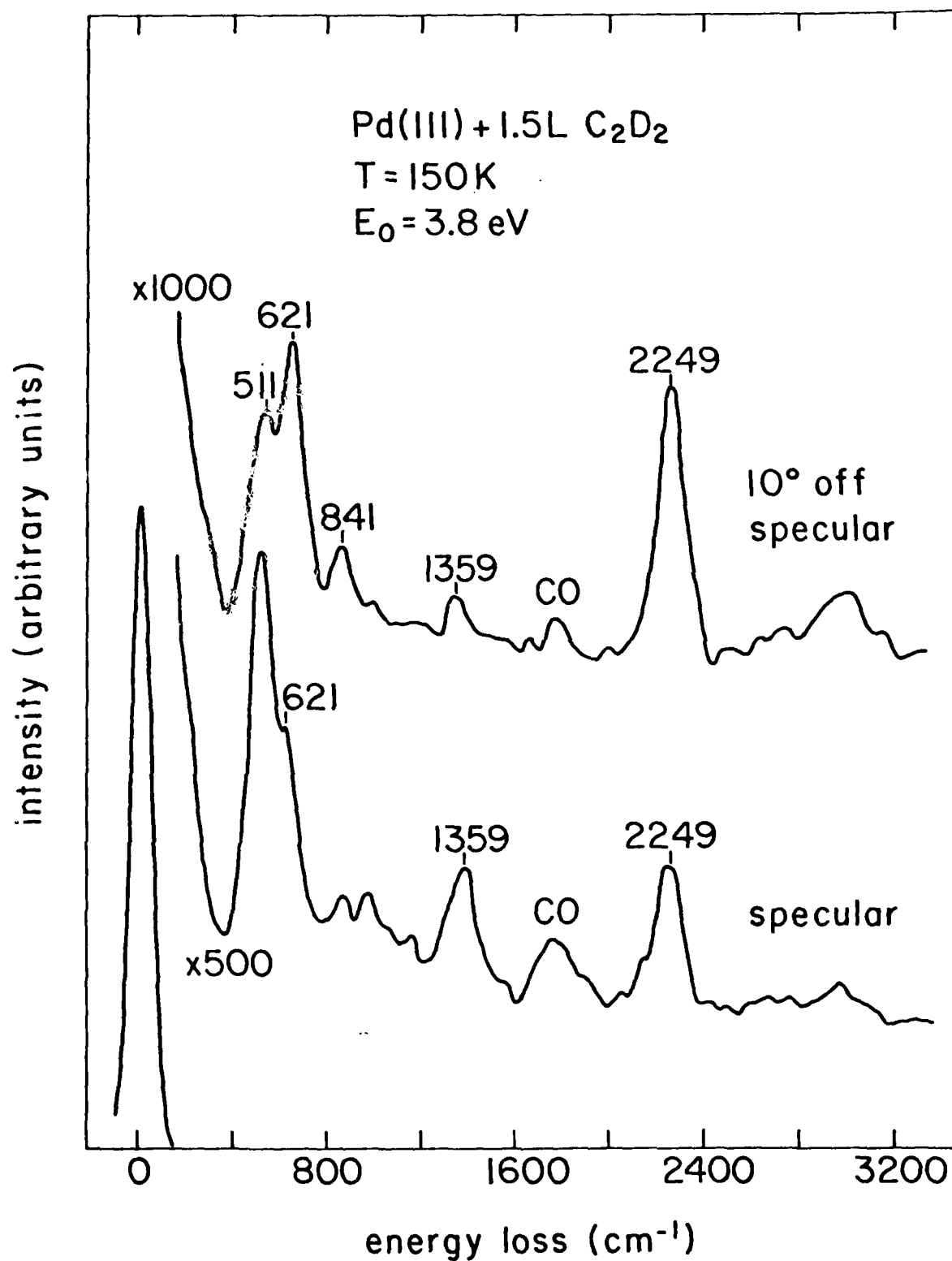


FIGURE 3

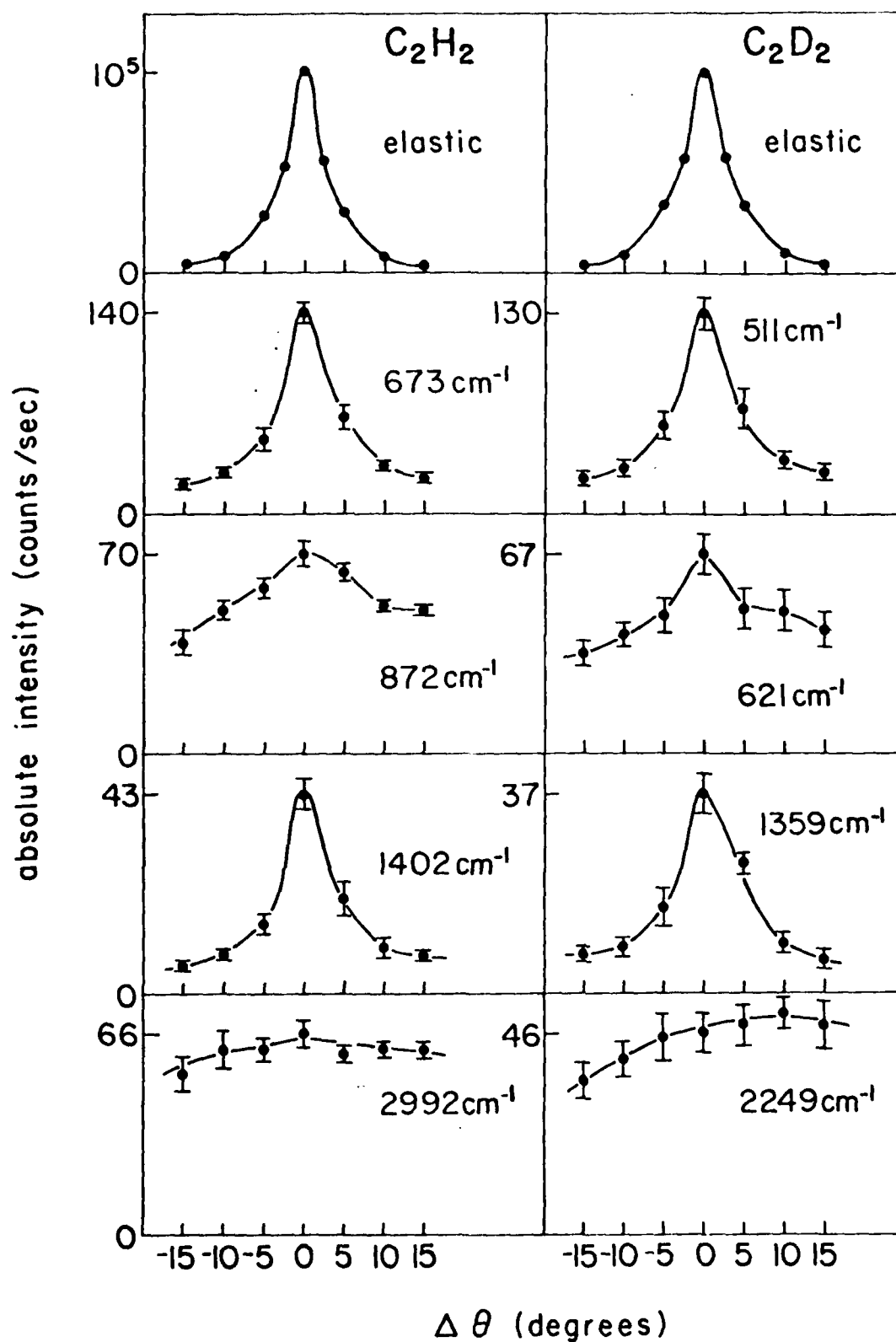


FIGURE 4

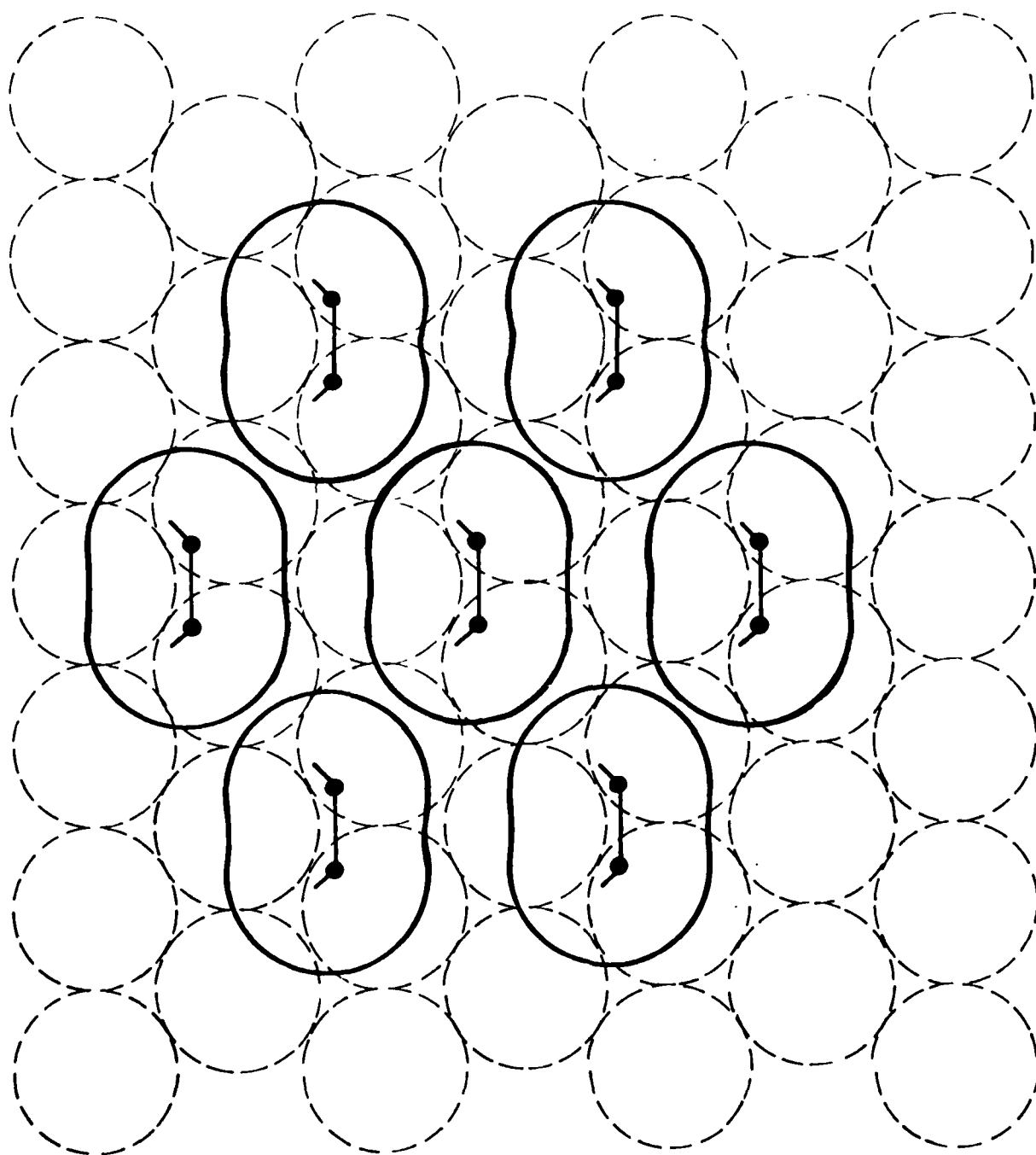


FIGURE 5

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